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Mass production of Al_2O_3 and ZrO_2 nanoparticles by hot-air spray pyrolysis

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ABSTRACT

Present work reports on the mass production of high surface area Al_2O_3 and ZrO_2 nanoparticles using inexpensive precursors (aluminium nitrate and zirconium oxy nitrate) developed from natural minerals (bauxite and zircon). Automated hot-air spray pyrolysis has been identified as suitable method for mass production of Al_2O_3 and ZrO_2 nanoparticles with high surface area and free flowing structure. The chemical purity, crystalline phase, size distribution, surface area and morphology of the produced nanoparticles are discussed in detail. Highly spherical cubic Al_2O_3 nanoparticles with an average particle size of 25 nm (d_{50}) and the specific surface area of 336 m^2g^{-1} were obtained. Subsequently, highly spherical monoclinic ZrO_2 nanoparticles with an average particle size of 30 nm (d_{50}) and the specific surface area of 280 m^2g^{-1} were obtained with the help of hot-air spray pyrolysis. The present automated experimental design yields 26–28 g of Al_2O_3 nanoparticles for the operation of the system for 8 h and yields 32–34 g of ZrO_2 nanoparticles for operation of the system for 10 h.

1. Introduction

Nanocrystalline ceramic oxides have attracted much attention due to their fundamental size dependent properties such as mechanical, physical, optical, and magnetic properties [1]. In fact, many nanocrystalline ceramic particles show unique electronic, magnetic and structural properties different from their bulk materials. The production of high surface area nanocrystalline ceramic particles gained momentum in advanced ceramics due to their potential applications in the densification of ceramics at lower sintering temperature and ultra fine grained ceramics [2]. Growing concern over the preparation of fine grained metal oxide nanocrystalline powders represents the cutting edge in many areas of advanced materials because of their unique material property and novel applications. Recently, much interest has been given on the preparation of nanocrystalline metal oxide ceramics due to their unique properties like high surface to volume ratio, chemical stability, heat resistance, and unique mechanical, electronic, magnetic, optical and catalytic properties.

More attentions have been made on Al_2O_3 and ZrO_2 nanoparticles in view of their large surface area which significantly enhances the mechanical, chemical and physical properties of the particles. Al_2O_3 is one of the most commonly used oxide ceramics for the packing of distillation tower, the catalyst of reactions and the additive of paints, pigments and ceramics [3,4]. Higher interaction surface area of ZrO_2 nanoparticles provides promising industrial applications such as catalyst supports [5], gas sensors [6], solid oxide fuel cells [7], biomaterials [8] and thermal barrier coating [9]. Bulk production of Al_2O_3 and ZrO_2 nanoparticles is essentially required for their extensive industrial applications.

A variety of synthesis methods are being explored and developed for the production of nano sized metal oxide particles [10,11]. Among many synthesis methods, precipitation, sol–gel, ball mill and spray pyrolysis are highly significant and useful techniques to produce mass quantity of nano metal oxides like Al_2O_3 and ZrO_2. Precipitation and sol–gel process have the advantage of high productivity but controlling of size is quite difficult. In addition, precipitation and sol–gel process yield aggregated and agglomerated particles with decreased specific surface area which requires post synthesis treatments like mechanical attrition and ball milling. On comparison with several synthesis methods, spray pyrolysis [12] has been found to be an ecofriendly method to produce the mass quantity of nanoparticles through continuous process. Spray pyrolysis is a powerful technique to synthesise a wide variety of ceramic nanoparticles like Al_2O_3 and ZrO_2. Large quantity of metal oxide particles with homogeneous particle and crystallite size less than 100 nano meters has been produced by this method. This is a simple method to allow continuous production of nano ceramic particles which offer the opportunity to tailor materials on a nano scale because of its small crystallites.

The present work focuses on the mass production of high surface area Al_2O_3 and ZrO_2 nanoparticles by hot-air spray pyrolysis using inexpensive precursors developed from natural minerals respectively bauxite and zircon sand. Hot-air spray pyrolysis is more effective and it provides a substantially wider spectrum of possibilities such as mass production with automated process, simple and inexpensive process, yielding high surface area particles with quite reduced particle size and free flowing structure. The present method helps in

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controlling the particle size and texture of Al_2O_3 and ZrO_2 nanoparticles. The present spray pyrolyser is an automated system which provides significant benefits such as scale up the productivity in a manufacturing environment. Further, these methods are used to achieve high purity products with less aggregated particles. It may be identified as the desirable method for large scale production of monodispersed Al_2O_3 and ZrO_2 nanoparticles with high surface area and quite uniform diameter.

2. Experimental section

2.1. Production of Al_2O_3 nanoparticles

2.1.1. Precursor synthesis

The synthetic Bayer liquor (sodium aluminium hydroxide) was extracted from raw bauxite using Bayer process. The detailed extraction process was given in our previous paper [10]. Bayer liquor is used as a precursor for the synthesis of Al_2O_3 nanoparticles. The extracted Bayer liquor (250 ml) was hydrolysed through drop by drop addition of 6 M HNO_3 (Merck GR, 69%) solution under constant stirring. An amorphous hydrated aluminium oxide was precipitated at pH 7. A characteristic white precipitate of $Al(OH)_3 \cdot H_2O$ appeared at this stage of the reaction. The obtained precipitate was filtered using Whatman (Grade No.: 40) filter paper and washed several times in double distilled and deionised water until it was free from sodium nitrate and unreacted components. Further, the precipitate ($Al(OH)_3 \cdot H_2O$) was dissolved in 500 ml of 1 M HNO_3 solution to obtain the aluminium nitrate solution. The schematic representation of the preparation of aluminium nitrate precursor was shown in Eqs. (1) and (2).

$$\underset{\text{Bayer liquor}}{NaAl(OH)_4 + HNO_3} \xrightarrow{\text{Precipitate}} \underset{\text{Precipitate}}{Al(OH)_3 \cdot H_2O + NaNO_3} \quad (1)$$

$$\underset{\text{Hydrated Aluminum Oxide}}{Al(OH)_3 \cdot H_2O + 3HNO_3} \xrightarrow{\text{Dissolution}} \underset{\text{Aluminium nitrate solution}}{Al(NO_3)_3 \cdot 4H_2O} \quad (2)$$

2.1.2. Hot-air spray pyrolysis

The perfect uniform solution of aluminium nitrate was used as the starting precursor in spray pyrolysis to get nano sized Al_2O_3 particles. The schematic diagram of automated spray pyrolysis experimental set-up used for mass production of nano Al_2O_3 particles is shown in Fig. 1. The present independent spray pyrolyser experimental set-up primarily consists of a) an atomiser which converts the starting solution into droplets, b) automated anti-blocking unit, c) tubular electric furnace with hot air blower, d) two fluid nozzle with compressed air inlet and sample feeding port, e) feed pump which facilitates the flow rate of precursor, f) reaction chamber, g) cyclonic sample collectors and h) purification system. The total process is automated using a single power control panel which controls the process automatically.

In spray pyrolysis, two stage reactions such as solvent evaporation and decomposition frequently take place in solution droplets. Fig. 2 shows the automated spray pyrolysis experimental set-up (Mini Modal Spray Pyrolyser, SM Scientech, Kolkata, India). Spray nozzle, stainless steel (AISI 316 L) tubular reaction chamber and hot air blower assembly are the fundamental processing parts of spray pyrolyser. The sprayer itself consists of two concentric nozzles (two fluid nozzle) with an outer nozzle of diameter 4 mm and an inner nozzle of diameter 1 mm. One end of the nozzle was connected to compressor air inlet and a reservoir (for holding the precursor) through silicone tube while other end of the nozzle was connected with tubular reaction chamber which inturn connected with hot air blower and cyclones. An aqueous aluminium nitrate precursor flowed into the inner nozzle through the peristaltic feed pump. The feed pump was used to control the flow rate of precursor. The feed rate was optimised and maintained as 0.2 L h^{-1}. Passage of the compressed air (30–40 psi) through the outer nozzle forced out the contents of the precursor in an inner nozzle. Thus, the precursor was

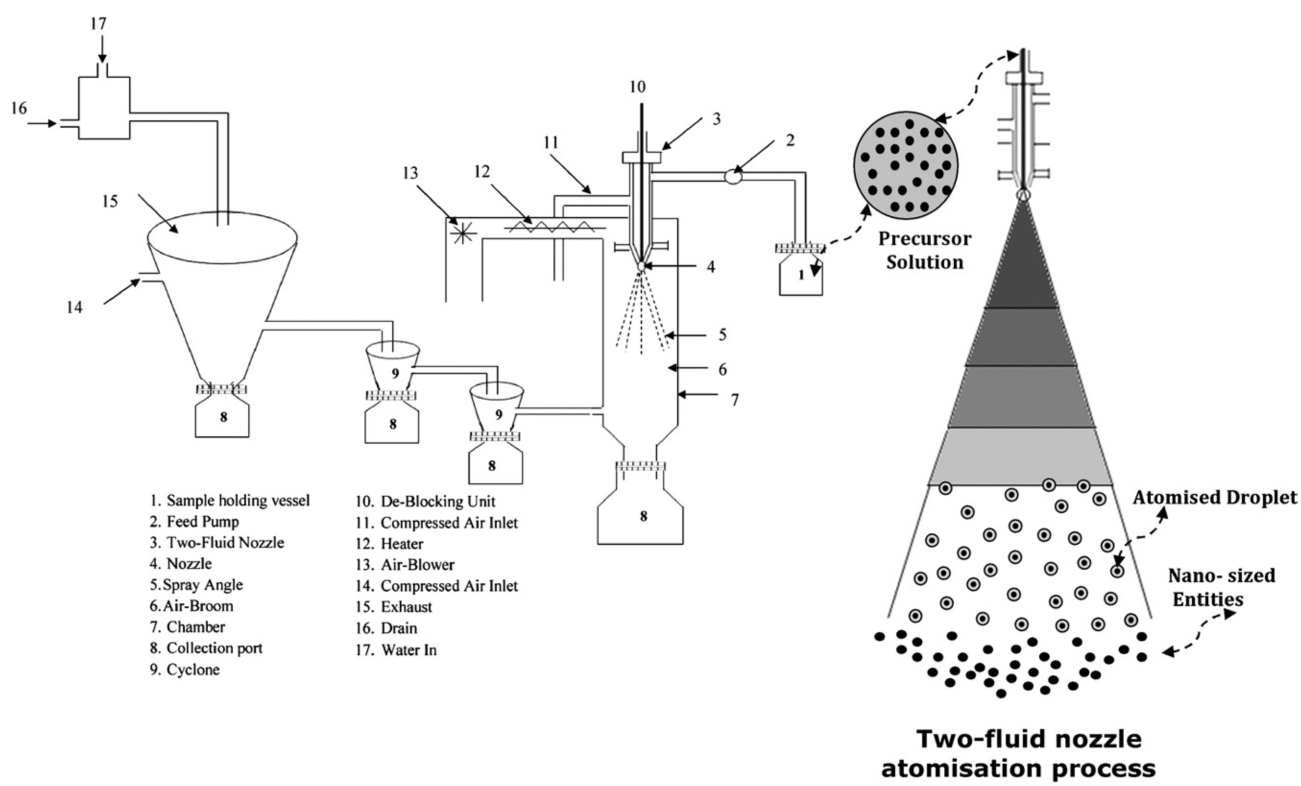

Fig. 1. Schematic diagram of automated spray pyrolysis experimental set-up.